

SOURCE CONTRIBUTIONS TO PM-2.5 IN AMBIENT AIR

PM-2.5 is a new air quality indicator and, consequently, there is a relative paucity of information on the sources of PM-2.5 and emission factors for estimating PM-2.5 emissions. There is, however, a fairly robust ambient monitoring database that includes information on the composition of ambient PM-2.5. That database provides important insights on the source contributions to ambient PM-2.5, even though none of the data were collected according to the PM-2.5 monitoring reference method. These data are taken largely from the Interagency Monitoring of Protected Visual Environments (IMPROVE) project. IMPROVE was designed to explore the current status and potential causes of visibility impairment in National Parks and other Class I areas; therefore, that database is most useful to explore the regional distribution of PM-2.5. A limited set of data that is more representative of urban conditions is also available and those data are useful to infer information about the differences between rural concentrations and urban area concentrations. Since the urban data represent only a select few urban locations, it is not possible to present a comprehensive assessment of urban PM-2.5 distributions. These data have been discussed in detail elsewhere. (Pace and Kuykendal, 1998) Summary pie charts showing the composition of measured ambient PM-2.5 are included in Appendix A to this report. Similar trends in sulfate concentrations between east and west, and relative magnitudes of sulfate and nitrate between urban and rural locations have also been observed in monitoring data collected across Canada. (Brook et al., 1997)

2.1 PRECURSORS TO SULFATE

Review of the figures in Appendix A reveals that sulfate is a significant component of PM-2.5 in the east and is less prevalent in the west. This is not unexpected since the east is strongly influenced by major sources of SO₂ from coal burning utilities in the Ohio Valley, Tennessee Valley, and along the east coast. Other industrial sources of SO₂ are also common in the east. There are also large sources of ammonia arising from major livestock production and fertilizer application throughout the Midwest, gulf coast, mid-Atlantic, and southeastern States, in addition to the sources of ammonia associated with human activities. Ammonia is usually involved in the formation of sulfate, but SO₂ can form sulfuric acid aerosols in the absence of ammonia. In addition, water vapor and radicals from photochemical systems are frequently found in the east. These conditions

combine to produce the observed large contributions of sulfate, on a percentage basis, at the eastern monitoring locations. In general, the sulfate fraction measured at eastern monitors ranges between 30% to 60% of the total PM-2.5 mass. For comparison purposes, the sulfate fraction measured at western monitors that are affected by fewer SO₂ sources rarely exceeds 20% of the total PM-2.5 mass. Sulfate, nitrate and some organics are hygroscopic and, therefore, contribute more to light scattering than some other PM-2.5 components. Sulfates are responsible for most of the visibility impairment in the Eastern United States. The contribution of sulfates to visibility impairment is less in the west as a result of lower relative humidity and the lower sulfate fraction of total PM-2.5 mass. On a mass concentration basis the relatively constant concentrations of sulfate in both urban and non-urban locations in the east, supports the conclusion that sulfate is regional in the east. In the west, however, some urban locations appear to have higher concentrations than either other urban locations or the non-urban locations.

2.2 PRECURSORS TO NITRATE

Many of the measurements used to produce the average patterns of nitrate mass that are discussed here may be influenced by a sampling artifact. Some of the nitrate mass initially collected on Teflon® or glass fiber filter media (as is done in the Federal Monitoring Reference Method) can volatilize during the sampling period. This artifact contributes to an artificially low nitrate mass in some samples. This problem will be corrected in the U.S. EPA's Speciation network by use of nylon filters that absorb the volatilized gaseous nitrate. The observed nitrate concentrations in the following discussion were collected using a variety of sampling protocols and thus some of the nitrate concentrations may be higher than would be expected had the FRM been used.

The principal sources of NO_x, motor vehicles and all fossil fuel combustion, are much more ubiquitous across the country and, as a result, there is no recognizable gradient in the percentage of ammonium nitrate concentrations from east to west. The nitrate fraction, as a percentage of observed PM-2.5 mass, is also generally lower than or approximately the same as the sulfate component, although in some areas in the west, the nitrate fraction can be greater than the sulfate fraction. One exception, illustrated in Appendix A, is for data collected in the San Joaquin Valley where agricultural sources of ammonia might combine with NO_x from normal combustion sources to increase the amount of ammonium nitrate. Based on the data summarized in Appendix A, the fraction of nitrate rarely exceeds 20% of the total PM-2.5 mass at any location. Urban locations generally have concentrations of nitrate that are higher than in non-urban locations, indicating that urban sources of nitrate precursors are important. Some areas in the west appear to have larger nitrate concentrations than are found in the east. This is due in part to a lower concentration for the sulfate precursor SO₂ in much of the west.

2.3 CARBONACEOUS PARTICLES

Carbonaceous particulate matter represents a significant fraction of the observed PM-2.5 in many locations. The data summarized in Appendix A show that in the east approximately 25% to 40% of the PM-2.5 is carbonaceous, and in the west carbonaceous particulate contributes between 50% and 75% of the mass of PM-2.5. There is a consistent trend of higher absolute concentrations or carbonaceous mass in urban areas relative to nonurban areas. These results imply that a significant amount of the carbonaceous particulate is related to urban sources. A distinction has been made between elemental carbon and organic carbon to refine the identification of the sources of total ambient PM-2.5 carbon. These two forms of carbon can arise from fundamentally different types of processes. Organic carbon emissions are associated primarily with low temperature combustion processes such as biomass burning, while elemental carbon emissions result mainly from high temperature combustion, such as diesel engines. Tracking the two forms of carbon particles separately enhances the resolving power of source apportionment techniques relative to those based solely on the total carbon fraction.

The distinction between elemental and organic carbon is based on the laboratory measurement methods commonly used to analyze PM-2.5 ambient air particulate filters for carbon. Although a variety of analytical schemes have been developed to distinguish between organic and elemental carbon (soot), all of the methods expose a portion of the filter to a carrier gas stream within a heated oven where the particulate carbon on the filter is converted to a gas (carbon dioxide or methane), which is then measured by a detector. Since organic carbon is released at a lower oven temperature than elemental carbon, the temperature dependence can be used to distinguish between the two classes of carbon.¹

Nearly one hundred percent of the elemental carbon observed in ambient samples results from primary particulate emissions from fossil fuel and some biomass combustion processes that achieve high temperatures. These particles are produced primarily in the size range of less than one μm in diameter. Recent source apportionment studies indicate that motor vehicle sources dominate the elemental carbon observed on ambient samples taken in urban settings, with emissions from diesel exhaust contributing between 50% and 70% of the elemental carbon mass concentration. (Watson et al., 1998) Gasoline

¹ Definition of elemental and organic carbon is included in the draft of the Speciation Guidance Document (found under "Speciation" section of the AMTIC Internet Homepage). The analytical method (NIOSH Method 5040) can be found in Birch, M.E., 1998. *Analyst*. 123:851-857.

powered vehicles contribute around 25% of the total and much of that results from automobiles that may not be maintained at optimum performance. Small contributions associated with road dust may include resuspended tire wear particles.

Organic carbon represents the remainder of carbon containing particulate matter. This fraction includes contributions from primary particle emissions, condensed particulate, and secondary particulate. Motor vehicle sources contribute up to 80% of the organic carbon mass in urban areas, although commercial cooking and wood burning can also represent significant contributions in many locations.

Total carbonaceous material appears to be a consistently high contribution to PM-2.5 ambient concentrations in all urban areas, although the total concentrations might be slightly elevated in western urban areas relative to eastern urban areas. In general, non-urban locations are characterized by similar concentrations everywhere.

A significant fraction of the organic carbon particle mass may also be HAPs. More work is needed to evaluate the HAP fraction of PM-2.5. Likewise, some portion of these carbonaceous particles are secondary - formed in the atmosphere from VOCs and semivolatile gaseous precursors. Current thinking is that this secondary organic component of fine carbonaceous particles is low compared to primary organic particles, but more research is needed.

2.4 GEOLOGICAL (CRUSTAL) PARTICLES

Geological particles become airborne when crustal materials are mechanically disturbed. While sources of crustal material contribute up to 85% - 90% of observed PM-10 concentrations, analyses of ambient samples reveals only small contributions (10% to 15%) of crustal material to the total PM-2.5 in most locations. That trend toward small contributions from crustal materials is also seen in the data collected in Canada. (Brook et al., 1997) The primary sources of crustal material are agricultural tilling, construction activities, road dust from both unpaved and paved roads, and windblown dust. Crustal material contains common metals including Al, Si, K, Fe, Ca, and other trace metals. It is not expected that sources of crustal material will be significant in terms of control strategies for PM-2.5 in most areas. Although concentrations of crustal materials are low everywhere, there is a slight increase in urban locations relative to non-urban locations, implying that road dust and construction sources may be important.

2.5 RELATIONSHIP BETWEEN SOURCE MAGNITUDE AND AMBIENT CONCENTRATION

Estimates of the emissions magnitude for some sources of PM-2.5 are sometimes inconsistent with the resulting ambient concentrations measured at nearby monitoring sites. This effect is observed most clearly with respect to surface fugitive dust sources of primary emissions. The causes for these discrepancies are being investigated at this time. One cause appears to be related to the source measurement methods that have been applied in some recent monitoring programs of area and line sources (e.g., agricultural tilling, unpaved roads, etc.). Frequently, the source emissions rate is estimated using a procedure that measures the horizontal flux of emissions through a vertical plane in the downwind direction very near to the source activity. That measurement is then compared to a similar estimate immediately upwind of the activity and the difference is used to calculate the emission rate.

While this technique is thought to provide an accurate estimate of the mass emissions rate from the source, the approach may not accurately account for other influences that can serve to remove a portion of that mass before it is entrained into the transport layer. For example, nearby vegetation or other physical structures may retain some of the mass. Additional mass could be removed by adhering to larger particles that are deposited close to the source through gravitational settling. One hypothesis is that the portion of the emissions mass that can be transported to monitor sites is limited to the mass that rises above surface features and becomes entrained into the local and/or regional wind flow pattern. This problem seems to be confined primarily to near surface sources of fugitive dust. Emissions from most point sources released from stacks, and other surface combustion sources may be affected by heat induced buoyancy that serves to elevate these emissions into the transport layer.

EPA is currently coordinating with the United States Department of Agriculture (USDA), the Forest Service, and other experts with experience in these processes to refine the emissions estimation methods for these sources. Currently, the mechanisms that produce fugitive emissions and affect the transport of those emissions to potential receptor sites are not well represented in the emissions estimation methods. Therefore, the confidence in PM-2.5 emissions estimates from fugitive dust sources is low. A similar removal mechanism may also affect near surface releases of NH_3 and other noncombustion related emissions of the gaseous precursors to secondary PM-2.5. (Duyzer, 1994)

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